ABSTRACT

It is becoming more and more problematic as nitrate levels in water sources are increasing which necessitates the development of its removal techniques. Nitrate may be transported in groundwater through soil or by rain and irrigation water. Additionally, fertilizers and pesticides used in the agricultural sector are the major sources of nitrate in groundwater.

The current work describes electrocatalytic removal of aqueous nitrate using different catalysts – Part 1: spatially suspended catalyst - (A) silver coated polyvinyl alcohol beads (Ag-PVA) catalyst; (B) silver metal particles (AgMPs) catalyst; and Part 2: cathode coated with cobalt oxide on titanium (Ti) plate (Ti/Co_3O_4) catalyst.

Firstly, silver-coated polyvinyl alcohol beads (Ag-PVA) as a catalyst were used for electrocatalytic nitrate removal. In this study, we concluded that nitrate removal was minimal in an undivided cell using graphite (Gr) as anode and iron (Fe) as cathode, restricted to 13% and 28% in the absence and presence of 6.67mM Ag-PVA beads, respectively. In both instances, TN (Total Nitrogen) removal was negligible. Nitrate and TN elimination in a divided cell was 70% and 12% in the absence of Ag-PVA beads, respectively, and increased to 85% and 52% in the presence of 6.67 mM Ag-PVA beads. In the divided cell with 6.67mM Ag-PVA beads, the elimination of nitrate proceeded in the following order: Fe > Ti > Cu > SS > Tin-coated Fe (Fe/Sn). Fe cathode produced little nitrite and maximum conversion to gaseous nitrogen (N_2-N). The effect of different operational parameters on the removal of nitrate in the divided cell was investigated, including the concentration of Ag-PVA beads (5mM, 6.67mM, and 8.33mM), the cathode material (SS, Cu, Ti, Fe, Tin-coated Fe (Fe/Sn)), the current density (5mA/cm^2, 10mA/cm^2, 15mA/cm^2 and 20mA/cm^2), the initial nitrate-N concentration (25mg/L, 50mg/L and 100mg/L), and the reusability of catalyst. The maximum removal of nitrate-N and N_2-N selectivity was attained at a catalyst concentration of 6.67 mM among various concentrations of Ag-PVA beads. The reduction of nitrate increased and selectivity for N_2-N improved when the current density was raised to 15 mA/cm^2. It seems that nascent hydrogen intercalation on Ag^0 results in the creation of reductive species that facilitate nitrate reduction. Ag-PVA beads could be reused for at least 8 times. .

Scanning electron microscope (SEM) and Energy-dispersive X-ray (EDAX) analysis of Ag-PVA beads revealed that most of the silver was immobilized on the outer surface of PVA beads. Nitrate removal in real groundwater was also studied. 85% nitrate removal in real water (groundwater) was achieved in the presence of 6.67mM Ag-PVA beads as compared to 53% in the absence of a catalyst.

Secondly, silver metal particles were used as catalyst for electrocatalytic removal of nitrate. In this investigation, nitrate removal was conducted in undivided and divided cells in the absence and presence of silver metallic particles (AgMPs). The removal of nitrate-N achieved in the absence of a catalyst and presence of 8mM AgMPs was 18% and 63% in 120min reaction time at a current density 10mA/cm^2 in an undivided cell utilising a mixed metal oxide (Ti/RuO_2) anode and titanium (Ti) cathode. Additionally, the removal of total nitrogen (TN) was nil in the absence of a catalyst and 15% in the presence of AgMPs in an undivided cell. Under identical experimental conditions, there was a considerable improvement in the removal of nitrate and TN in a divided cell, which went from 77% and 23%, respectively, in the absence of a catalyst to 99% and 60%, in the presence of 8mM AgMPs. The effect of various factors on the removal of nitrate in the divided cell was investigated, including the concentration of AgMPs (4mM, 6mM, 8mM, 10mM, 14mM, and 20.8mM), the inter-electrode distance (3cm, 5.5cm, and 7.7cm), the cathode material (SS, Cu, Ti, Fe, Tin-coated Fe (Fe/Sn)), the current density (5mA/cm^2, 10mA/cm^2 and 15mA/cm^2), the initial nitrate-N concentration (25mg/L, 50mg/L and 100mg/L), and the reusability of catalyst. Ti > Fe > Cu > SS > Fe/Sn was the order in which nitrate was eliminated in a divided cell in the presence of 8mM AgMPs using various cathode materials. With the least amount of nitrite-N and ammonia-N formation, the Ti cathode in the presence of 8mM AgMPs resulted in the highest conversion to nitrogen gas. As the current density rose to 10 mA/cm^2, the selectivity toward nitrogen gas improved and overall nitrate reduction improved. Nascent hydrogen intercalation on metallic silver seems to facilitate the catalytic nitrate reduction by generating reductive species (AgH_x). AgMPs were reusable up to 10 times.

Thirdly, a Ti plate coated with cobalt oxide (Ti/Co_3O_4) was employed as a cathode in a divided cell for the removal of high concentration of nitrate removal in a simulated metal-finishing wastewater. Various factors influencing nitrate removal were studied, including

initial nitrate-N concentration (500mg/L, 750mg/L, and 1000mg/L), current density (10mA/cm^2, 20mA/cm^2 and 30mA/cm^2) and reusability of Ti/Co_3O_4. 95% nitrate-N removal was achieved with 20.8% ammonia-N generation and 72.75% N_2-N generation at 750mg/L of initial nitrate-N concentration at 20mA/cm^2 current density in 180min of electrolysis time. The reusability of coated catalyst Ti/Co_3O_4 was about 12 times. Further, struvite formation was studied with an aim to remove the residual ammonia-N. The effect of various molar ratios of Mg:NH_4:PO_4 (0.8:1:0.8, 1:1:1, 1.5:1:1, 1:1:1.5 and 1.5:1:1.5) on struvite formation for ammonia removal were studied at pH 9. The ammonia concentration remaining after the struvite formation was within the industrial wastewater discharge limits. X-ray Diffraction (XRD) analysis revealed that struvite formed in the current study matched with the pure struvite. It was also noted that various metals in the simulated metal-finishing wastewater were almost completely removed by precipitation during electrocatalytic nitrate removal.

Keywords : Electrocatalytic reduction, Nitrate-N, Nitrite-N, Ammonia-N, Nitrogen-N, Selectivity, Ag-PVA beads, AgMPs, Ti/Co_3O_4, Reusability